Molecular Wires Acting as Coherent Quantum Ratchets

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The effect of laser fields on the electron transport through a molecular wire being weakly coupled to two leads is investigated. The molecular wire acts as a coherent quantum ratchet if the molecule is composed of periodically arranged, asymmetric chemical groups. This setup presents a quantum rectifier with a finite dc-response in the absence of a static bias. The nonlinear current is evaluated in closed form within the Floquet basis of the isolated, driven wire. The current response reveals *multiple* current reversals together with a nonlinear dependence (reflecting avoided quasi-energy crossings) on both, the amplitude and the frequency of the laser field. The current saturates for long wires at a nonzero value, while it may change sign upon decreasing its length.

More than two decades after the idea of a molecular rectifier [1], the experimental and theoretical study of such systems presently enjoys a vivid activity [2]. Recent experimental progress has enabled the reproducible measurement [3, 4] of weak tunneling currents through molecules which are coupled by chemisorbed thiol groups to the gold surface of the leads. A necessary ingredient for future technological applications will be the possibility to control *a priori* the tunneling current through the molecule. Advances in that very direction have lately been achieved by the development of a molecular field-effect transistor [5]. Typical energy scales in molecules are in the optical and the infrared regime, where basically all of the today's lasers operate. Hence, lasers represent an inherent possibility to control atoms or molecules and possibly currents through them.

A particularly intriguing phenomenon in strongly driven systems is the so-termed ratchet effect [6, 7, 8, 9], originally discovered for overdamped classical Brownian motion in cyclic asymmetric nonequilibrium systems. Counterintuitively to the second law one then observes a directed transport although all acting forces possess *no* net bias. This effect has been established as well within the regime of dissipative, incoherent quantum Brownian motion [10]. With this work we investigate the possibilities for quantum wires to act as a coherent quantum ratchet, i.e. we consider the coherent quantum transport through molecular wires with a saw-tooth like level structure of the orbital energies when subjected to the influence of a strong laser field.

Recent theoretical descriptions of molecular conductivity are based on a scattering approach [11, 12], or assume that the underlying transport mechanism is an electron transfer reaction from the donor to the acceptor site and that the conductivity can be derived from the corresponding reaction rate [13]. It has been demonstrated that both approaches yield identical results in a large parameter regime [14]. Within the high-temperature limit, the electron transport on the wire can be described by inelastic hopping events [13, 15].

Atoms and molecules in strong oscillating fields have been widely studied within a Floquet formalism [16, 17]. This suggests the following procedure: Making use of the tools that have been acquired in that area, we develop a formalism that combines Floquet theory for a driven molecule with the many-particle description of transport through a system that is coupled to ideal leads. This approach is devised much in the spirit of the Floquet-Markov theory [18, 19] developed for driven dissipative quantum systems. Technically, we thereby work beyond the usual rotating-wave approximation as frequently employed, such as e.g. in Ref. [20].

The lead-molecule model.— The total system composed of the driven wire, the leads, and the molecule-lead couplings is described by the Hamiltonian

$$H(t) = H_{\text{wire}}(t) + H_{\text{leads}} + H_{\text{wire-leads}} \qquad (1)$$

The wire itself is modelled by N atomic orbitals $|n\rangle$, $n = 1, \ldots, N$, which are in a tight-binding description coupled by hopping matrix elements. The Hamiltonian for the electrons on the wire reads

$$H_{\text{wire}}(t) = \sum_{n,n'} H_{nn'}(t)\, c_n^\dagger c_{n'}, \qquad (2)$$

where the fermionic operators c_n, $c_n^\dagger$ annihilate, respectively create, an electron in the atomic orbital $|n\rangle$. The influence of the laser field is given by a periodic time-dependence of the on-site energies yielding a single particle Hamiltonian of the structure $H_{nn'}(t) = H_{nn'}(t+\mathcal{T})$, where $\mathcal{T} = 2\pi/\Omega$ is determined by the angular frequency Ω of the laser field.

The orbitals at the left and the right end of the molecule, that we shall refer to as donor and acceptor states, $|D\rangle = |1\rangle$ and $|A\rangle = |N\rangle$, respectively, are coupled to ideal leads (cf. Fig. 1) by the tunneling Hamiltonian

$$H_{\text{wire-leads}} = \sum_q (V_{qL}\, c_{qL}^\dagger c_D + V_{qR}\, c_{qR}^\dagger c_A) + \text{h.c.}, \qquad (3)$$
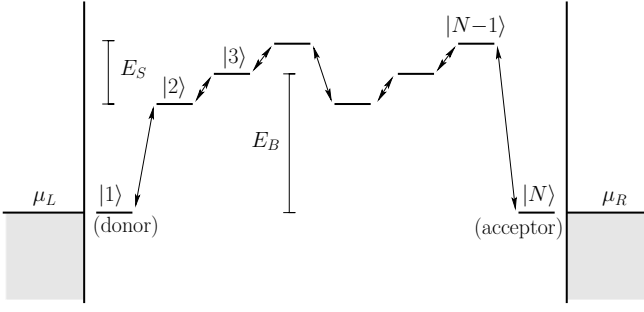
FIG. 1: Level structure of the wire ratchet with $N = 8$ atomic sites, i.e. $N_g = 2$ asymmetric molecular groups. The bridge levels are E_B above the donor and acceptor levels and are shifted by $\pm E_S/2$.

where c_{qL} (c_{qR}) annihilates an electron in state Lq (Rq) on the left (right) lead. In the following we will assume a wide-band limit $\Gamma_{L/R} = (2\pi/\hbar) \sum_q |V_{qL/R}|^2 \delta(\epsilon - \epsilon_{qL/R})$, i.e. an energy-independent coupling strength.

The leads themselves are modelled by grand-canonical ensembles of electrons with the Hamiltonian $H_\text{leads} = \sum_q (\epsilon_{qL} c_{qL}^\dagger c_{qL} + \epsilon_{qR} c_{qR}^\dagger c_{qR})$ and electro-chemical potentials $\mu_{L/R}$. Then the only non-trivial expectation values of lead operators are $\langle c_{qL}^\dagger c_{qL} \rangle = f(\epsilon_{qL} - \mu_L)$, where ϵ_{qL} is the single particle energy of the state qL and correspondingly for the right lead. Here, $f(\epsilon) = (1 + e^{\epsilon/k_B T})^{-1}$ is the Fermi function.

Perturbation theory.— While the dynamics of the leads and the wire, including the external driving, will be treated exactly, we take the wire-lead Hamiltonian as a perturbation into account. From the Liouville-von Neumann equation $i\hbar\dot\varrho(t) = [H(t), \varrho(t)]$ for the total density operator $\varrho(t)$ one obtains by standard techniques the master equation

$$\dot\varrho(t) = -\frac{i}{\hbar}[H_\text{wire}(t) + H_\text{leads}, \varrho(t)] \tag{4}$$
$$-\frac{1}{\hbar^2}\int_0^\infty d\tau [H_\text{wire-leads}, [\widetilde{H}_\text{wire-leads}(t - \tau, t), \varrho(t)]].$$

The tilde denotes operators in the interaction picture with respect to the molecule and the lead Hamiltonian without the molecule-lead coupling, $\widetilde{X}(t,t') = U_0^\dagger(t,t')\, X\, U_0(t,t')$, U_0 is the propagator without the coupling. The net (incoming minus outgoing) electrical current through the left contact is given by the time-derivative of the electron number in the left lead multiplied by the electron charge $-e$. From Eq. (4) follows in the wide-band limit the expression

$$I_L(t) = e\, \text{tr}[\dot\varrho(t) N_L] = e\frac{\Gamma_L}{\pi\hbar} \text{Re} \int_0^\infty d\tau \int d\epsilon\, e^{i(\epsilon+\mu_L)\tau/\hbar}$$
$$\times f(\epsilon)\langle [c_1, \tilde{c}_1^\dagger(t - \tau, t)]_+ \rangle - e\Gamma_L \langle c_1^\dagger c_1 \rangle \tag{5}$$

and *mutatis mutandis* for the net current through the right contact. Equation (5) expresses the current by the expectation values $\langle [c_n, \tilde{c}_n(t - \tau, t)]_+ \rangle$ and $\langle c_n^\dagger c_n \rangle$. We emphasize that these quantities depend on the dynamics of the isolated wire and are thus influenced by the driving.

Floquet decomposition.— Let us now focus on the driven molecule decoupled from the leads. Since its Hamiltonian is periodic in time, $H_{nn'}(t) = H_{nn'}(t + \mathcal{T})$, $\mathcal{T} = 2\pi/\Omega$, we can solve the time-dependent Schrödinger equation within a Floquet approach, i.e. we make use of the fact that there exists a complete set of solutions of the form $|\Psi_\alpha(t)\rangle = e^{-i\epsilon_\alpha t/\hbar}|\Phi_\alpha(t)\rangle$ with the quasi-energies ϵ_α. The so-called Floquet modes $|\Phi_\alpha(t)\rangle$ obey the time-periodicity of the driving field and can thus be decomposed in a Fourier series: $|\Phi_\alpha(t)\rangle = \sum_{k=-\infty}^{\infty} e^{-ik\Omega t}|\Phi_{\alpha,k}\rangle$. These obey the quasienergy equation [16, 21, 22]

$$\left(\sum_{n,n'}|n\rangle H_{nn'}(t)\langle n'| - i\hbar\frac{d}{dt}\right)|\Phi_\alpha(t)\rangle = \epsilon_\alpha|\Phi_\alpha(t)\rangle. \tag{6}$$

To make use of the knowledge about the driven molecule that we obtain from Floquet theory, we define the Floquet representation of the fermionic creation and annihilation operators by the time-dependent transformation

$$c_\alpha(t) = \sum_n \langle \Phi_\alpha(t)|n\rangle c_n, \tag{7}$$
$$c_n = \sum_\alpha \langle n|\Phi_\alpha(t)\rangle c_\alpha(t). \tag{8}$$

The back transformation (8) follows from the mutual orthogonality and the completeness of the Floquet states at equal times [16]. It is now straightforward to prove that $\tilde{c}_\alpha(t - \tau, t) = c_\alpha(t)\exp(i\epsilon_\alpha\tau/\hbar)$. This yields a spectral decomposition of Eq. (5), which makes it possible to evaluate the time and energy integrations therein. Averaging $I_L(t)$ over the driving period [23] leads to our first main result, namely the average current

$$\bar{I} = \frac{e\Gamma_L}{\hbar} \sum_{\alpha k} \Big[\langle \Phi_{\alpha,k}|D\rangle\langle D|\Phi_{\alpha,k}\rangle f(\epsilon_\alpha + k\hbar\Omega - \mu_L)$$
$$- \sum_{\beta k'} \langle \Phi_{\alpha,k'+k}|D\rangle\langle D|\Phi_{\beta,k'}\rangle R_{\alpha\beta,k} \Big], \tag{9}$$

where $R_{\alpha\beta}(t) = \langle c_\alpha^\dagger(t)c_\beta(t)\rangle = \sum_k e^{-ik\Omega t}R_{\alpha\beta,k}$. Here we have used the fact that the $R_{\alpha\beta}(t)$ are expectation values of a dissipative, periodically driven system. Therefore, they share in the long-time limit the time-periodicity of the driving field and can be represented by a Fourier series.

The remaining task in computing the stationary current is to find the Fourier coefficients $R_{\alpha\beta,k}$ at asymptotic times. For that purpose, we derive from the master equation (4) an equation of motion for the $R_{\alpha\beta}(t)$.

Since all coefficients of the master equation as well as its asymptotic solution are $\mathcal{T}$-periodic, we can split it into its Fourier components which have to satisfy Eq. (4) separately. Finally, we obtain for the $R_{\alpha\beta,k}$ the inhomogeneous set of equations

$$\frac{i}{\hbar}(\epsilon_\alpha - \epsilon_\beta + k\hbar\Omega)R_{\alpha\beta,k} \qquad (10)$$

$$= \frac{\Gamma_L}{2}\sum_{k'}\Big\{\sum_{\beta'k''}\langle\Phi_{\beta,k''+k'}|D\rangle\langle D|\Phi_{\beta',k''+k}\rangle R_{\alpha\beta',k'}$$

$$+ \sum_{\alpha'k''}\langle\Phi_{\alpha',k''+k'}|D\rangle\langle D|\Phi_{\alpha,k''+k}\rangle R_{\alpha'\beta,k'}$$

$$- f(\epsilon_\alpha + k'\Omega - \mu_L)\langle\Phi_{\beta,k'-k}|D\rangle\langle D|\Phi_{\alpha,k'}\rangle$$

$$- f(\epsilon_\beta + k'\Omega - \mu_L)\langle\Phi_{\beta,k'}|D\rangle\langle D|\Phi_{\alpha,k'+k}\rangle\Big\}$$

$$+ \big(\Gamma_L, \mu_L, |D\rangle\langle D|\big) \rightarrow \big(\Gamma_R, \mu_R, |A\rangle\langle A|\big).$$

For the typical parameter values used below, a large number of side-bands contributes significantly to the Fourier decomposition of the Floquet modes $|\Phi_\alpha(t)\rangle$. Numerical convergence for the solution of the master equation (10), however, is already obtained by using a few side-bands for the decomposition of $R_{\alpha\beta}(t)$. This keeps the numerical effort relatively small and justifies the use of the Floquet representation (8). Yet we are able to treat the problem *beyond* the usual rotating-wave-approximation [20], which in certain parameter regimes turns out to be crucial [24].

Ratchet wire.— We consider a molecular wire that consists of a donor and an acceptor site and N_g asymmetric molecular groups (cf. Fig. 1). Each of the $N = 3N_g + 2$ orbitals is coupled to its nearest neighbors by a hopping matrix elements Δ. The laser field renders each level oscillating in time with a position dependent amplitude. Then the time-dependent wire Hamiltonian reads

$$H_{nn'}(t) = [E_n - A\cos(\Omega t)\, x_n]\,\delta_{nn'} - \Delta(\delta_{n,n'+1} + \delta_{n+1,n'}),$$
$$(11)$$

where $x_n = (N+1-2n)/2$ is the scaled position of site n, the energy A equals electron charge multiplied by laser field strength and distance between two neighboring sites, and Δ is the hopping matrix element. The energies of the donor and the acceptor orbitals are assumed to be at the level of the chemical potentials of the attached leads and since no voltage is applied, $E_1 = E_N = \mu_L = \mu_R$. The bridge levels E_n lie at E_B and $E_B \pm E_S/2$, respectively, as sketched in Fig. 1. We remark that for the sake of simplicity intra-atomic dipole excitations are neglected within our model Hamiltonian (11).

In our numerical studies, we use the hopping matrix element Δ as the energy unit; in a realistic molecule, Δ is of the order $0.1\,\text{eV}$. Thus, our chosen wire–lead hopping rate $\Gamma = 0.1\Delta/\hbar$ yields $e\Gamma = 2.56 \times 10^{-5}\,\text{Ampère}$ and $\Omega = 3\Delta/\hbar$ corresponds to a laser frequency in the infrared. Note that for a typical distance of 2Å between two
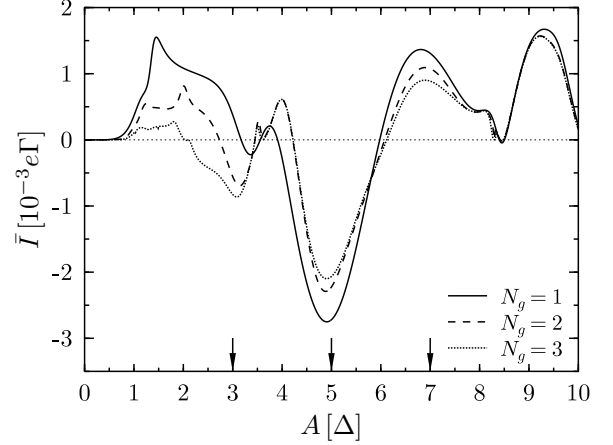

FIG. 2: Time-averaged current (in arbitrary units) through a molecular wire that consists of N_g bridge units as a function of the driving strength A. The bridge parameters are $E_B = 10\Delta$, $E_S = \Delta$, the driving frequency is $\Omega = 3\Delta/\hbar$, the coupling to the leads is chosen as $\Gamma_L = \Gamma_R = 0.1\Delta/\hbar$, and the temperature is $k_BT = 0.25\Delta$. The arrows indicate the driving amplitudes used in Fig. 3.

neighboring sites, a driving amplitude $A = \Delta$ is equivalent to an electrical field strength of $2 \times 10^6\,\text{V/cm}$.

Figure 2 shows the stationary time-averaged current $\bar{I}$. In the limit of a very weak laser field, we find $\bar{I} \propto E_S A^2$ (not shown). This behavior is expected from symmetry considerations: The asymptotic current must be independent of any initial phase of the driving field and therefore is an even function of the field amplitude A. This indicates that the ratchet effect can only be obtained from a treatment beyond linear response. For strong laser fields, we find that $\bar{I}$ is almost independent of the wire length. If the driving is intermediately strong, $\bar{I}$ depends in a short wire sensitively on the driving amplitude A and the number of asymmetric molecular groups N_g: even the sign of the current may change with N_g, i.e. we find a current reversal as a function of the wire length. For long wires that comprise five or more wire units, the average current becomes again length-independent, as can be seen from Fig. 3. This identifies the observed current reversal as a finite size effect. The fact that $\bar{I}$ converges to a finite value if the number of wire units is enlarged, demonstrates that the dissipation caused by the coupling to the leads is sufficient to establish the ratchet effect in the limit of long wires. In this sense, no on-wire dissipation is required.

Figure 4 depicts the average current *vs.* the driving frequency Ω, exhibiting resonance peaks as a striking feature. Comparison with the quasi-energy spectrum reveals that each peak corresponds to a non-linear resonance between the donor/acceptor and a bridge orbital. While the broader peaks at $\hbar\Omega \approx E_B = 10\Delta$ match the 1:1 res-
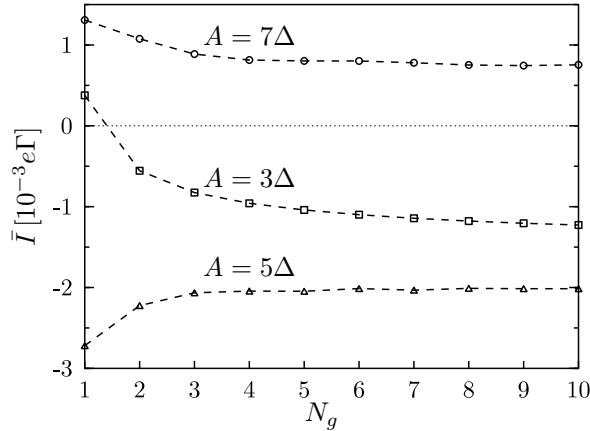
FIG. 3: Time-averaged current (in arbitrary units) as a function of the number of bridge units N_g for the laser amplitudes indicated in Fig. 2. All other parameters are as in Fig. 2. The connecting lines serve as a guide to the eye.
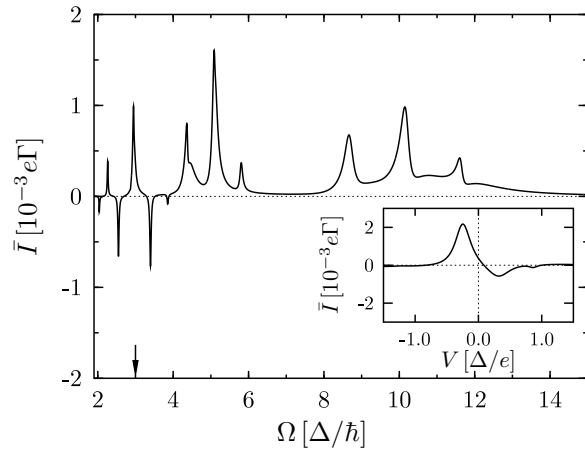

FIG. 4: Time-averaged current (in arbitrary units) as a function of the driving frequency Ω for $A = \Delta$ and $N_g = 1$. All other parameters are as in Fig. 2. The inset displays the dependence of the average current on an externally applied static voltage V, which we assume here to drop solely along the molecule. The driving frequency is $\Omega = 3\Delta/\hbar$ (cf. arrow in main panel).

onance (i.e. the driving frequency equals the energy difference), one can identify the sharp peaks for $\hbar\Omega \lesssim 7\Delta$ as multi-photon transitions. Owing to the broken spatial symmetry of the wire, one expects an asymmetric current-voltage characteristic. This is indeed the case as depicted in the inset of Fig. 4.

With this work we put forward an approach for the computation of the current through a molecular wire in the presence of laser fields of arbitrary strength. Our method is based upon the Floquet solutions of the isolated driven wire. The technique is seemingly also very

efficient for larger wire systems. With this formalism at hand, we have established the possibility of using molecular wires as coherent quantum ratchets. As a finite size effect, the wire may exhibit a characteristic current reversal as a function of (decreasing) length; upon increasing the wire length the average current rapidly converges to a finite value. The strong dependence on the driving parameters in turn admits a tailored quantum control of current with respect to both its sign and its magnitude. In particular, this driven molecular wire with the distinctive multiple current reversal feature encompasses new prospects to pump and shuttle electrons on the nanoscale in an *a priori* manner. Our physical estimates show that a realization of a molecular wire ratchet indeed is within experimental reach.

[1] A. Aviram and M. A. Ratner, Chem. Phys. Lett. **29**, 277 (1974).
[2] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature **408**, 541 (2000).
[3] X. D. Cui *et al.*, Science **294**, 571 (2001).
[4] J. Reichert *et al.*, cond-mat/0106219.
[5] J. H. Schön, H. Meng, and Z. Bao, Nature **413**, 713 (2001).
[6] P. Hänggi and R. Bartussek, *Lecture Notes in Physics*, edited by J. Parisi, M. S. C., and W. W. Zimmermann (Springer, Berlin, 1996), Vol. 476, pp. 294–308.
[7] R. D. Astumian, Science **276**, 917 (1997).
[8] F. Jülicher, A. Adjari, and J. Prost, Rev. Mod. Phys. **69**, 1269 (1997).
[9] P. Reimann, Phys. Rep. (in press).
[10] P. Reimann, M. Grifoni, and P. Hänggi, Phys. Rev. Lett. **79**, 10 (1997).
[11] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 8649 (1994).
[12] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, 1995).
[13] A. Nitzan, Ann. Rev. Phys. Chem. **52**, 681 (2001); and references therein.
[14] A. Nitzan, J. Phys. Chem. A **105**, 2677 (2001).
[15] E. G. Petrov and P. Hänggi, Phys. Rev. Lett. **86**, 2862 (2001).
[16] M. Grifoni and P. Hänggi, Phys. Rep. **304**, 219 (1998).
[17] N. L. Manakov, V. D. Ovsiannikov, and L. P. Rapoport, Phys. Rep. **141**, 319 (1986).
[18] R. Blümel *et al.*, Phys. Rev. Lett. **62**, 341 (1989).
[19] S. Kohler, T. Dittrich, and P. Hänggi, Phys. Rev. E **55**, 300 (1997).
[20] C. Bruder and H. Schoeller, Phys. Rev. Lett. **72**, 1076 (1994).
[21] J. H. Shirley, Phys. Rev. **138**, B979 (1965).
[22] H. Sambe, Phys. Rev. A **7**, 2203 (1973).
[23] Owing to charge conservation, the time-averages of the two net currents $I_{L,R}(t)$ equal each other.
[24] J. Lehmann, S. Kohler, and P. Hänggi (to be published).